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(19) (CA) **CANADIAN PATENT** (12)

(54) Composition for Minimizing Fouling of Heat Exchangers
and Other Hydrocarbon Processing Equipment

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1. Introduction

The first part of the paper discusses the importance of the research and the objectives of the study. It also provides a brief overview of the methodology used in the study. The second part of the paper presents the results of the study and discusses the implications of the findings. The third part of the paper concludes the study and provides some suggestions for future research.

The results of the study show that there is a significant positive correlation between the variables studied. This finding is consistent with the previous research in this area. The implications of the findings suggest that the variables studied are important factors in the process being studied. The study also provides some suggestions for future research, which include the need for further investigation into the relationship between the variables studied and the need for more detailed data collection.

COMPOSITION FOR MINIMIZING FOULING OF HEAT
EXCHANGERS AND OTHER HYDROCARBON PROCESSING EQUIPMENT

Field of The Invention

10 This invention relates to methods of inhibiting fouling by injecting an antifoulant composition into a stream of a hydrocarbonaceous material scheduled to be heated in a reboiler, heat exchanger, process heater, or the like. A heat exchanger and resultant products column are able to function for longer periods of time when such fouling inhibitor minimizes the formation of deposits in the heat exchanger.

BACKGROUND

20 Fouling of petroleum processing equipment occurs continuously during the period when petroleum or its derivatives are being processed in the equipment. Generally, fouling is caused by the gradual buildup of a layer of polymeric material resulting from the thermal polymerization of unsaturated materials which are present in the material processed. Ultimately fouling becomes a problem of such magnitude that it becomes necessary to take the equipment out of service for cleaning. Cleaning is an expensive, time consuming operation and consequently methods of preventing fouling, or at least significantly reducing the rate of fouling, are constantly being sought. The most economical method of reducing the fouling rate in process equipment is to add chemicals which inhibit fouling, called "antifoulants", to the feed stream being processed.

Diene compounds such as butadiene undergo undesired spontaneous polymerization (i.e., polymerization of monomers due to heat or the random generation of free radicals in the monomers)

during storage, shipping or processing. The problem is particularly acute during purification operations at elevated temperatures such as in distillation. Spontaneous polymerization is disadvantageous not only because it causes fouling of equipment used for processing diene monomer, but also because it usually renders the monomer unfit for use. Accordingly, a need exists for an agent which serves to inhibit the spontaneous polymerization of diene monomers during their processing.

Prior Art

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U.S. Patent 3,148,225 to Albert employs dialkylhydroxylamine for inhibiting popcorn polymers in SBR rubbers. Prior workers have understood that dialkylhydroxylamine compounds react with free radicals to prevent undesired formation of polymers. Further inhibition of popcorn polymerization is effected by Gross (U.S. Patent 3,426,063) by use of an arylhydroxylamine. U.S. Patent 2,965,685 to Campbell discloses inhibition of vinyl aromatic monomer polymerization by using from 5 ppm to 5 percent dialkylhydroxylamine in the vinyl aromatic monomer. Furthermore, Mayer-Mader (U.S. Patent 3,878,181) teaches termination of an aqueous emulsion polymerization of chloroprene or dichlorobutadiene by addition of diethylhydroxylamine and Sato (U.S. Patent 3,849,498) discloses that diethylhydroxylamine is effective as a polymerization inhibitor for alcoholic solutions of unsaturated aldehydes. U.S. Patent 3,392,204 to Elmer discloses that styrene can be stabilized against polymerization by dosing with a small amount of a diethylhydroxylamine salt of certain carboxylic acids.

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Although some of the published literature concerned with antifoulant compositions suggest that some antifoulants might also serve to inhibit the thermal polymerization of unsaturated

components of the hydrocarbonaceous liquid subjected to elevated temperatures, there has been no pattern of transfer of technology from the polymer inhibition field to antifoulant composition technology.

Gerbrand (U.S. Patent 4,386,224) discloses that the color of alkyl phenols can be stabilized and discoloration inhibited by the presence of a small amount of diethylhydroxylamine.

Albert (U.S. Patent 3,333,001) stabilized dialkylhydroxylamines themselves by use of mercaptobenzothiazole.

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U.S. Patent 4,400,368 (Zaida) discloses a method of removal of hydrogen sulfide and carbon dioxide from sour gases by contacting the sour gases with an aqueous solution of certain polyvalent metal chelates. The chelate life is taught to be improved by the presence of a stabilizing amount of certain nitrogen compounds including, inter alia, diethylhydroxylamine.

Miller (U.S. Patent 3,105,810) describes the use of amine salts of dodecyl benzene sulfonic acid as surfactant useful in antifoulant compositions. Gonzales (U.S. Patent 3,271,295) discloses substituted succinic imides as surfactants in antifoulant compositions.

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Waldby (U.S. Patent 3,340,160) discloses an olefin polymerization inhibitor which is an aqueous solution of an alkali metal nitrite and a quinoid, amino, nitro or phenol compound. Among the amino compounds contemplated by Waldby are N,N-di-n-butylhydroxylamine, 2,4-diaminodiphenylamine, diethanolamine and monoethanolamine.

In certain olefin processing operations it is desirable to have an antifoulant or polymerization inhibitor which participates between the oil and water phase. In other words, a single inhibitor

acting in both the oil and water phase would be desirable over adding separate water-soluble and oil-soluble inhibitors.

Accordingly, it is an object of the present invention to provide an antifoulant which acts in both the aqueous phase and the hydrocarbon phase of a water-containing hydrocarbon processing operation. It is another object of the present invention to present a method of enhancing antifoulant protection for equipment in those operations. These and other objects of the invention are set forth in the following description and examples of the invention.

10 Summary of The Invention

The improved antifoulant effects afforded by the present invention are achieved by injecting into a stream of diene hydrocarbon scheduled for fractionation, distillation or other processing, a fouling preventing amount of a lower hydroxylamine, i.e., diethylhydroxylamine.

Detailed Description

20 At least one major and significant advantage associated with the use of lower dialkylhydroxylamines has been overlooked extending their applications in diene process applications. This includes their partition coefficient between hydrocarbon and water.

The advantage of lower dialkylhydroxylamines is based on the partition coefficient of the dialkylhydroxylamine in the presence of water. As an example, aqueous diethylhydroxylamine has a partition coefficient of 13:1 in favor of water. Therefore, approximately 93% of diethylhydroxylamine would be extracted from an organic process stream which may come into contact with water through washing or which has water present as the result of accumulation as tank bottoms water. Although this factor has been a limiting factor in efforts to translate the use of dialkyl-

hydroxylamines into a majority of hydrocarbon processing units, where there is either a water wash or caustic wash unit upstream of the hydrocarbon distillation units, it has now been discovered that diethylhydroxylamine (DEHA) serves as an effective antifoulant and polymerization inhibitor in diene treatment operations, most notably for butadiene treatment.

10 In butadiene applications, the crude butadiene distillation train is run at temperatures in the range of 90-175°F under pressure conditions of 50-180 psig. Under these temperature and pressure conditions, DEHA will not flash overhead with the desired butadiene products of production, thus enabling production of purified monomer without inhibitor present. Further, inhibition of undesired fouling deposits in the lower portions of the column is achieved as well as inhibition of formation of resinous-like polymer glasses in the heat exchangers and reboilers.

20 The polymerization inhibitor (DEHA) of the invention can be introduced into the diene monomer to be protected by any conventional method. It is generally introduced just upstream of the point of desired application by an suitable means such as by the use of a proportionating pump. The DEHA polymerization inhibitor may be added as a concentrate but it is preferable to add it as a solution which is compatible with the diene monomer being treated. Suitable solvents are water (if a cosolvent such as an amine or N-methyl pyrrolidone is used), alcohols (provided their boiling point is sufficiently high as to not be distilled overhead into the final recovered product), acetonitrile and other organic solvents which have boiling points higher than butadiene. Concentration of DEHA polymerization inhibitor in the solvent is desirably in the range of about 10 to 90 weight percent and
30 preferably about 30 to 80 weight percent based on the total weight of DEHA and solvent.

The DEHA is used at a concentration which is effective to provide the desired protection against spontaneous polymerization. It has been determined that amount of DEHA in the range of about 100-250 ppm based on the weight of the diene monomer being treated affords ample protection against undesired polymerization. For most applications the inhibitor is used in amounts in the range of about 5 to 500 ppm.

Furthermore, fouling due to both hydrocarbon phases and aqueous phases can sometimes be enhanced by use of an antifouling blend of DEHA and an oil soluble hydroxylamine such as di-n-butylhydroxylamine.

The following examples will serve to further illustrate without limiting the invention.

Example I

Conventional butadiene recovery units processing approximately 93% crude butadiene to obtain a final product containing 99.5% butadiene by column distillation with the operating conditions in the last of three columns being overhead 65 psig, 118°F, and 85 gpm product butadiene to storage, have been forced to shut down periodically (every 190 days) to clean reboilers and the column because of butadiene fouling. Injection of a sodium nitrite solution at the rate of 5 gpm to the reflux return of the column did not enhance run times. Certain hydrocarbon and water soluble inhibitors were screened in the laboratory and found to be less effective than diethylhydroxylamine (see Table I) against styrene which was employed as a model because of its ease of handling.

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Table I

Test	Observation of Polymerization 1000 ppm Inhibitor, 140°F
no inhibitor	1
phenylenediamine	1
tert-butyl catechol 3	1
diethanolamine	1
diethylhydroxylamine	2
1) popcorn polymer growth began after 2 days; extensive growth after 4 days	
2) no growth in 11 days	
3) previously had tried a phenol/catechol on unit without success	

Example II

To determine the effectiveness of various hydroxylamines, the same test was repeated. Results are shown below in Table II.

Table II

Test	Conc (ppm)	Observation of Polymerization
no inhibitor	none	polymer formed in 12 hrs at 100°F
(a) DEHA	100	6 days at 100°F
(b) di-isopropyl-hydroxylamine	160	6 days at 100°F
(c) di-n-butylhydroxyl-amine	170	6 days at 100°F

Finally, the solubility characteristics of compounds (a) and (c) above were determined; dibutylhydroxylamine was found to be oil soluble not water soluble unless salted with a mineral acid or short chain carboxylic acid. Diethylhydroxylamine -- as previously mentioned -- can be made oil or water soluble but partitions in favor of water.

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EXAMPLE III

As evidenced by Example I, the addition of a purely oil-soluble inhibitor proved unsatisfactory. The addition of a water-soluble oxygen scavenger used to inhibit polymerization also proved unsatisfactory. However, the addition of a hydroxylamine which can partition or the addition of a blend of hydroxylamines (one water soluble, one oil soluble) offered superior performance.

10 To the same unit as in Example I, 250 ppm DEHA based on the weight of the butadiene monomer being processed, was added to the overhead reflux of the final product column of the three columns in series with the same operating conditions as in Example I.

The column treatment extended the run time from 190 days in two previously untreated runs to 308 days, a 62% increase.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In an improved process for purifying diene monomers by inhibiting equipment fouling wherein the purification is by distillation, wherein the improvement comprises adding a polymerization inhibiting amount of diethylhydroxylamine to the monomer being purified prior to distillation, during distillation or both.

2. The process according to claim 1 wherein the diene monomer is butadiene.

3. The process according to claim 1 wherein diethylhydroxylamine is added to the monomer in an amount of from 5 to 500 ppm based on the weight of diene monomer treated.

4. The process according to claim 1 wherein the purification process includes a water wash or water scrubbing stream and fouling of equipment contacted by both hydrocarbon and water phases is inhibited by a polymerization inhibiting blend of diethylhydroxylamine and di-n-butylhydroxylamine.



1. The first part of the document is a letter from the President of the United States to the Congress, dated January 3, 1862.

2. The second part is a report from the Secretary of the Treasury, dated January 10, 1862.

3. The third part is a report from the Secretary of the Interior, dated January 10, 1862.

4. The fourth part is a report from the Secretary of the War, dated January 10, 1862.

5. The fifth part is a report from the Secretary of the Navy, dated January 10, 1862.

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Abstract of The Disclosure

In an improved process for purifying diene monomers by inhibiting equipment fouling wherein the purification is by distillation, wherein the improvement comprises adding a polymerization inhibiting amount of diethylhydroxylamine to the monomer being purified prior to distillation, during distillation or both.

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